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(FILE 'HOME' ENTERED AT 13:45:00 ON 30 DEC 2003)

FILE 'CA' ENTERED AT 13:45:20 ON 30 DEC 2003

L1 1586 S MODULAT?(1A) (MOLECUL? OR PHOTOLY? OR PHOTODIS?)
L2 97 S L1 AND (UV OR ULTRAVIOLET)
L3 21 S L2 AND (CONCENTRAT? OR COMPUTER OR MICROPROC?)
L4 67 S L1 AND (NO2 OR NOX OR (NITROGEN OR NITRIC) (1A) (OXIDE OR MONOXIDE OR
DIOXIDE))
L5 25 S L1 AND (O3 OR OZONE)
L6 5 S L4 AND L5
L7 24 S L4-5 AND CONCENTRAT?
L8 6 S L2 AND APPARATUS
L9 44 S L3, L6-8
L10 38 S L9 NOT PY>1999
L11 36 S L10 NOT (ANIMAL OR MOUSE OR MICE OR BIO?)
L12 33 S L11 NOT (VESICLE OR HOLO?)
L13 30 S L12 NOT (MAGNETIC RESONANCE OR LINE STRENGTH)

=> d bib, ab 1-30 l13

L13 ANSWER 2 OF 30 CA COPYRIGHT 2003 ACS on STN

AN 126:22237 CA

TI Recent improvements in atmospheric trace gas monitoring using mid-infrared tunable diode lasers

AU Nelson, David D.; Zahniser, Mark S.; McManus, J. Barry; Shorter, Joanne H.; Wormhoudt, Joda C.; Kolb, Charles E.

CS Aerodyne Research, Inc., Billerica, MA, 01821, USA

SO Proceedings of SPIE-The International Society for Optical Engineering (1996), 2834 (Application of Tunable Diode and Other Infrared Sources for Atmospheric Studies and Industrial Process Monitoring), 148-159

AB A review, with 21 refs., that discusses recent advances in our techniques for monitoring atm. trace gases using lead salt liq. nitrogen-cooled diode lasers. Our approach employs an optical system with all reflective optics. Our closed path systems rely on a proprietary astigmatic multipass cell to achieve long optical path lengths in a low-vol. sampling cell. We have also developed open-path systems which we have used for remote sensing of automobile and aircraft engine exhaust. Our data acquisition method uses rapid frequency sweeping (~3 kHz), followed by nonlinear least-squares anal. of the retrieved spectrum. Recent advances include an emphasis on multi-laser multispecies detection systems, such as simultaneously monitoring the **nitric oxide**, carbon monoxide, and carbon dioxide **concns.** in automobile exhaust plumes. Other advances are focused on achieving improved detection sensitivity. In support of this goal, we have demonstrated astigmatic multipass cells with very long optical paths, we have improved the nonlinear least-squares spectral fitting routines allowing them to fit complex multi-peak spectra (fingerprint fitting), and we have introduced **photolytic modulation** as a method to discriminate spectra of photolytically active species (HClO, NO2) from background absorption and optical interference fringes. These techniques are being applied to the monitoring of a wide variety of atm. mols. including CH4, CO, CO2, N2O, NO, NO2, HNO2, HNO3, O3, and HClO.

L13 ANSWER 6 OF 30 CA COPYRIGHT 2003 ACS on STN

AN 111:123548 CA

TI Peroxy radical reactions in the photooxidation of acetaldehyde

AU Moortgat, Geert K.; Cox, Richard A.; Schuster, Gerhard; Burrows, John P.; Tyndall, Geoffrey S.

CS Air Chem. Div., Max-Planck-Inst. Chem., Mainz, D-6500, Fed. Rep. Ger.
SO Journal of the Chemical Society, Faraday Transactions 2: Molecular and
Chemical Physics (1989), 85(7), 809-29
AB The behavior of reactants, products and radical intermediates during the
photooxidn. of CH₃CHO at room temp. and 700 Torr pressure was studied using
a novel **app.** The **app.** consists of a double multi-path spectrometer,
combining both IR and UV absorption spectrometry with the addnl. capability
of **modulated photolysis** for transient detection. Photooxidn. of CH₃CHO gave
CO, CO₂, H₂O, CH₂O, HCOOH, CH₃OH, CH₃OOH, CH₃COOH and CH₃COOOH as
identifiable products by long-path FTIR spectrometry. The effect of
variation of the **concn.** of O and CH₃CHO upon the different photolysis
products was studied, and **computer** simulation of exptl. data was used to
test a proposed mechanism contg. 50 elementary reactions. Absorption vs.
time profiles at selected wavelengths in the 210-275 nm region were recorded
in the **modulated photolysis** of CH₃CHO-air mixts. Transient absorptions were
assigned to peroxy radicals, and kinetic anal. of the data assisted by
computer simulation resulted in a value $k_{10} = 4.8 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for
the reaction HO₂ + CH₃O₂ → products. This value is somewhat higher than the
value $k_{10a} = 3.5 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction HO₂ + CH₃O₂ → CH₃OOH
+ O₂ obtained from the **computer** simulations of Me hydroperoxide formation,
indicating that an addnl. product channel may occur.

L13 ANSWER 8 OF 30 CA COPYRIGHT 2003 ACS on STN
AN 109:99454 CA
TI Kinetics of the reaction of nitrate radical with hydroperoxo
AU Hall, Ian W.; Wayne, Richard P.; Cox, Richard A.; Jenkin, Michael E.;
Hayman, Garry D.
CS Phys. Chem. Lab., Univ. Oxford, Oxford, UK
SO Journal of Physical Chemistry (1988), 92(17), 5049-54
AB The kinetics of the title reaction were investigated by **mol. modulation-UV**
visible absorption spectroscopy. NO₃ and HO₂ were generated by **modulated**
photolysis of Cl₂ in the presence of ClONO₂, H₂, and O₂ in a flow system at
1 atm pressure and their **concn.** modulations were monitored by time-resolved
absorption at 662 and 220 nm, resp. The rate coeff. for the overall
reaction NO₃ + HO₂ → products, k_4 , was detd. by **computer** fitting to data at
5 temps. in the range 263-338 K. An upper limit of 0.6 for the ratio k_{4b}/k_4
at 283 K, where k_{4b} is the rate const. for the reaction channel NO₃ + HO₂ →
OH + NO₂ + O₂, was established by measurement of OH by modulated resonance
absorption. The alternate channel, 4a, produces HNO₃.

L13 ANSWER 20 OF 30 CA COPYRIGHT 2003 ACS on STN
AN 91:217508 CA
TI Kinetics of chlorine oxide radical reactions using **modulated photolysis**.
Part 1. Disproportionation of chlorine monoxide in the dichlorine
photosensitized decomposition of **ozone**
AU Cox, R. Anthony; Derwent, Richard G.
CS Environ. Med. Sci. Div., AERE, Harwell, OX11 0RA, UK
SO Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry
in Condensed Phases (1979), 75(7), 1635-47
AB The formation and decay of ClO radicals and OClO in mixts. of Cl₂ and O₃ in
O₂ photolyzed at 298 K by square-wave modulated light were monitored using a
time-resolved UV spectrophotometer. Quantum yields for the Cl-
photosensitized decompn. of O₃ were detd. also. ClO decayed by 3 parallel
bimol. reactions to Cl₂ + O₂, Cl + ClOO, and Cl + OClO and rate consts. for
these reactions were detd. by **computer** simulation of the exptl. **concn.**-time
measurements for ClO, OClO, and O₃. The considerable departure from 2nd-
order kinetics under **modulated photolysis** was interpreted in terms of
formation of ClOOCl, which is sufficiently stable at 298 K to be kinetically

significant. The equil. const. for the dimerization of ClO was estd. to be $\sim 10^{-14}$ cm³/mol. at 298 K.

L13 ANSWER 21 OF 30 CA COPYRIGHT 2003 ACS on STN
AN 91:45056 CA
TI Kinetics of the reaction $\text{HO}_2 + \text{NO}_2 (+\text{M}) = \text{HO}_2\text{NO}_2$ using molecular modulation spectrometry
AU Cox, R. A.; Patrick, K.
CS Environ. Med. Sci. Div., A.E.R.E., Harwell/Oxon., OX11, UK
SO International Journal of Chemical Kinetics (1979), 11(6), 635-48
AB Rate consts. for the reaction $\text{HO}_2 + \text{NO}_2 (+\text{M}) = \text{HO}_2\text{NO}_2 (+\text{M})$ were obtained from direct observations of the HO_2 radical by using the technique of mol. modulation UV spectrometry. HO_2 was generated by periodic photolysis of Cl_2 in the presence of excess H_2 and O_2 , and k_1 was detd. from the measured concns. and lifetime of HO_2 with NO_2 present. k_1 increased with pressure in the range of 40-600 torr, and a simple energy transfer model gave the following limiting 2nd- and 3rd-order rate consts. at 283 K: $k_{1\infty} = 1.5 \pm 0.5 \times 10^{-12}$ cm³ mol.⁻¹ s⁻¹ and $k_{1\text{III}} = 2.5 \times 10^{-31}$ cm⁶/mol.⁻² s. The UV adsorption spectrum of peroxyntitric acid was also recorded in the range of 195-295 nm; it showed a broad feature with a max. at 200 nm, $\sigma_{\text{max}} = 4.4 \times 10^{-18}$ cm² mol.⁻¹.

L13 ANSWER 29 OF 30 CA COPYRIGHT 2003 ACS on STN
AN 67:68959 CA
TI Molecular-modulation spectrometry. I. New method for observing infrared spectra of free radicals
AU Johnston, Harold Sledge; McGraw, Gary E.; Paukert, Thomas T.; Richards, Lorenzo Willard; Van den Bogaerde, J.
CS Univ. of California, Berkeley, CA, USA
SO Proceedings of the National Academy of Sciences of the United States of America (1967), 57(5), 1146-53
AB A method for observing the ir spectrum of free radicals at very low concns. that applies at moderate light intensities is described. The method is based on the mol. modulation technique. The photolyzing light is turned on and off continually, and the concn. of the reactants, intermediates, and products is thereby modulated to a slight extent. When the concn. of a chem. species is varied in a periodic fashion, the absorption which is due to this species is used to modulate a transmitted ir beam intensity. The interesting range of light intensity is 10¹⁴ to 10¹⁶ photons/cm²-sec., and this intensity is readily obtained by uv fluorescent lamps or low-pressure Hg arcs. At these light intensities, the expected concn. of radicals is $\sim 10^{10}$ to 10¹³/cc. and the lifetime of the radicals is ~ 0.1 -10 sec. The ir path length is 80 m. The degree of modulation of the beam ($-dI/I$) is 10⁻⁴ for typical situations; thus it is desirable to detect a modulation as low as 10⁻⁶. By scanning through the ir spectrum, the light intensity is modulated only when one passes through that ir region characteristic of the absorption by a particular radical, reactant, or product. Expts. for the detection of ClO and HO₂ radicals are carried out.

=> log y

STN INTERNATIONAL LOGOFF AT 14:01:05 ON 30 DEC 2003